Protective Coatings for Space System Components Fabricated Using Ionic Self Assembled Monolayer Processes

Final Scientific and Technical Report

Reporting Period: 1 October 1997 to 31 October 1997

BMDO SBIR Phase I Contract No. N00014-97C-0227

Technical Monitor: John Pazik

Submitted to: Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5660

Prepared by: Michael Miller
F&S Inc.
2801 Commerce Street
Blacksburg, VA 24062

Mike Miller
Principal Investigator

Yanjing Liu
Senior Scientist

Richard O. Claus
Subcontract PI

F&S, Inc.

TABLE OF CONTENTS

1.0 Executive Summary

The objective of this 6-month BMDO Phase I SBIR program is to develop robust, protective coatings for space-based and other DoD materials and structures, and to develop the plan for their commercialization for military and commercial applications.

F&S is using novel ionic self-assembled monolayer (ISAM) processes for the fabrication of nanoparticle-based protective coatings. The ISAM process allows the simple and low-cost formation of multifunctional coatings with excellent uniformity on different material surfaces of different sizes and irregular shapes at room temperature and pressure. The focus of this program is to develop and demonstrate ISAM-processed coatings with good thermal stability, abrasion resistance, electromagnetic interference (EMI) shielding and other properties required by space-based and other DoD structures, as well as by related non-DoD commercial product applications.

Accomplishments during the final month of this program (October 1 – October 31, 1997) include the following items that are summarized in this report.

- Obtained additional information concerning coating requirements
- Developed methods to improve coating properties based on selected nanoparticles and thin-film self-assembly methods
- Extended measurements of abrasion resistance of coatings
- Characterized Al_2O_3 ionic solutions and ionic self-assembled Al_2O_3 nanocomposite thin-films
- Extended characterization of platinum nanoparticles
- Extended conductivity, I/V and C/V measurements
- Completed coating product commercialization planning

This program parallels another separate BMDO Phase I program in which F&S is using ISAM processes to develop and commercialize nanoparticle-based electronic and optoelectronic microdevices for space-based and other military systems. Dr. Colin Wood at ONR is the monitor of that program. Although these programs are directed at totally different applications and commercial markets, they overlap in the need to develop conductive multi-layer thin-films that can serve as both EMI shielding layers and patterned electronic interconnects. Both of these BMDO programs build on prior F&S and Virginia Tech work with ARO (Dr. Robert Reeber) and current Virginia Tech DURIP program support from ARO (Dr. John Prater).

2.0 Project Task Review

The technical tasks proposed by F&S as key to the development and commercialization of ISAM-processed protective nanoparticle coatings are summarized as follows.

Task 1 - Review the performance metrics of protective coatings for optical and structural components that may be implemented using organic/inorganic ISAM thin-films. Determine quantitative requirements on mechanical robustness, spectral transmission and other required

functionalities. The results of this task are being used to set the coating and process chemistry goals for the entire coating development and product commercialization program.

Task 2 - Identify the full range of inorganic nanoparticles and polymer molecules that together can give the fabricated ISAM coating mechanical and thermal robustness as well as desired optical, electromagnetic and other multifunctional properties. This is building on prior Virginia Tech research experience in ISAM design and synthesis.

Task 3 - Develop the precursor aqueous solution chemistries required to obtain uniform suspensions of desired anions and cations in solution. This is based on recent ISAM research results with inorganic particles that are particularly difficult to process, such as TiO_2, Fe_3O_4 and ZrO_2, in combination with high-performance polymers, such as water soluble polyimides. These results have been obtained with assistance from the NSF High Performance Polymer Center and faculty in the Department of Chemical Engineering at Virginia Tech.

Task 4 - Fabricate prototype protective coatings using existing ISAM fabrication facilities at Virginia Tech and developed facilities at F&S.

Task 5 - Quantitatively characterize the fabricated ISAM coatings using available materials analysis testing facilities to demonstrate thin-film structure, UV transmission/absorption, electromagnetic skin depth, thermal behavior, abrasion resistance and other properties.

Task 6 - Consider how the ISAM process could be used to fabricate other types of coatings and nanoscale devices and systems. We anticipate this leading to large-scale commercial markets in spacecraft and aircraft coatings, electronic and optical devices, and high-performance magnetic coatings for data storage applications. This task overlaps in part with that of a parallel BMDO Phase I SBIR program to develop ISAM-processed nanoparticle-based electronic and optoelectronic microdevices.

Task 7 - Develop the technical plan for upscaling ISAM coating production volume and coated substrate size, and the accompanying business plan for commercialization and marketing. Litton is directly assisting F&S with this task.

This report briefly describes progress made on each of these tasks during the sixth month of this program and reviews accomplishments of the entire Phase I program.

3.0 Task Schedule

Monthly work schedule goals are outlined in Table 3-1. The most important new results of work in each month are as follows.

COMPLETED

May	• demonstration of ISAM nanoparticle coating process on silica
June	• initial quantitative analysis of coating properties and degradation
July	• demonstration of protective ISAM coatings on polycarbonate
August	• demonstration of ultra-abrasion resistant ZrO_2 nanoparticle coatings
September	• feasibility study of protective ISAM coatings on polymer composites
October	• demonstration of abrasion resistant Al_2O_3 and Au nanoparticle coatings
	• completion of product commercialization plan

The project is on schedule as of 31 October 1997.

ID	Task Name	Duration	Start
1	Set Coating Metrics	27.2w	Thu 5/1/97
2	ID Candidate Nanoparticles	136d	Thu 5/1/97
3	TiO2 and Fe3O4 Nanopar	23d	Thu 5/1/97
4	ZrO2/Abrasion Resistant	45d	Sun 6/1/97
5	Nanoparticles	66d	Fri 8/1/97
6	Develop ISAM Precursors	136d	Thu 5/1/97
7	TiO2 and Fe3O4	23d	Thu 5/1/97
8	ZrO2/Abrasion Resistant	9w	Sun 6/1/97
9	Other Nanoparticles	13.2w	Fri 8/1/97
10	Fabricate ISAM Films	136d	Thu 5/1/97
11	On Glass and Polymers	23d	Thu 5/1/97
12	Coatings on Metal	23d	Tue 7/1/97
13	On Polymer Composites	21d	Fri 8/1/97
14	Other Substrates	45d	Mon 9/1/97
15	Characterization	136d	Thu 5/1/97
16	Large/Irregular Substrate	23d	Thu 5/1/97
17	Thermal/Abrasion Degra	52d	Sun 5/25/97
18	Conductivity/Permeabilit	100d	Sun 6/1/97
19	Adaptive Signature	79d	Tue 7/15/97
20	ID Other Nanoparticle Uses	13.2w	Fri 8/1/97
21	Commercialization Plan	27.2w	Thu 5/1/97

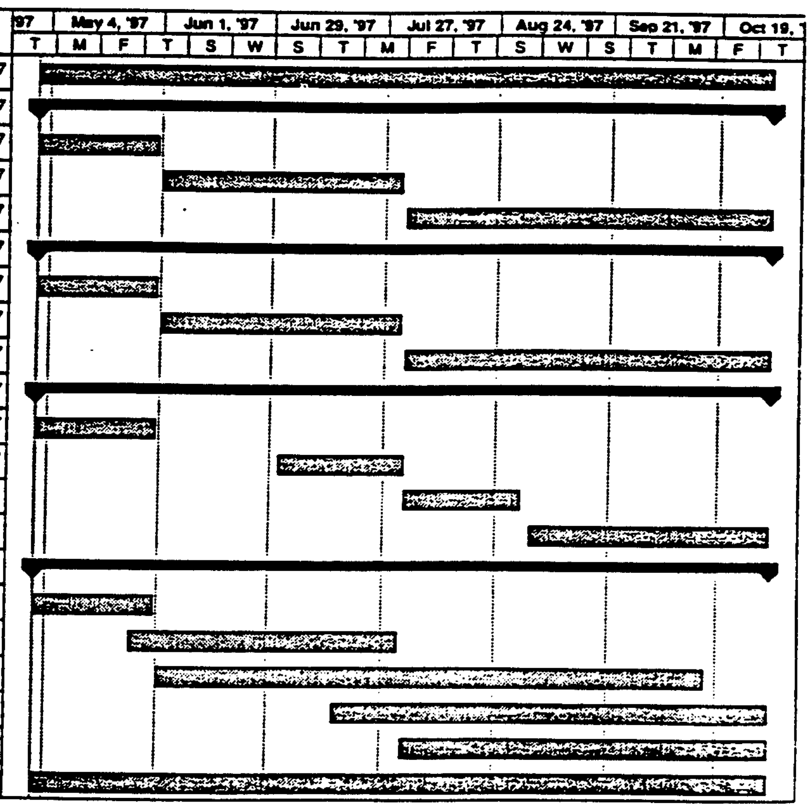


Table 3-1. Primary Monthly Work Schedule Goals.

4.0 Review of Accomplishments

This section briefly reviews accomplishments during final month of the six-month BMDO Phase I SBIR project and summarizes accomplishments of the previous five months.

4.1 Requirements on Coating Materials

Determining and updating requirements for inorganic/organic nanoparticle/polymer-based systems has been performed extensively during the entire 6-month Phase I program. A large number of government laboratory and industrial scientists and engineers have been consulted by telephone and by personal visits, and many have visited either FEORC or F&S to discuss technical developments and methods of cooperation.

Government agency staff contacted and briefed concerning this program have included researchers and program managers at BMDO, DARPA, ONR, AFOSR, ARO, NRL, NRaD, Wright Laboratory, Phillips Laboratory, NIST, NSF and NAWC. Company researchers briefed include individuals at Litton, IDA, Lockheed-Martin Astronautics, Lockheed-Martin Research Laboratories, Northrop-Grumman, Boeing, TACAN, GE, 3M, Alcatel, Lucent and other companies.

During the last month of the program, the following additional efforts were made to more clearly define coating material requirements for BMDO, other DoD and commercial applications.

- Extended literature survey to determine how to best approach Phase II process development and prototype product demonstration tasks.
- Visited by GE Corporate R&D staff on 6 October to discuss possible GE use of protective UV blocking coatings on polycarbonate aircraft canopies manufactured by GE, and high-temperature ISAM nanoparticle coatings of potential use in many GE products.
- Visited by ETA Inc. president and staff on 13 October to discuss use of protective ISAM coatings on eyewear for corrective eye diagnostics and treatment.
- Continued discussions (R. Claus) on 15 October with Mariah Vision Inc. concerning potential use of protective ISAM-formed coatings on optical system surfaces.
- Visited (R. Claus) Newport News Shipbuilding on 22 October to discuss possibility of ISAM-fabricated corrosion protection coatings on shipboard components and systems.
- Discussion (R. Claus) with B. F. Goodrich Aerospace Chief Scientist concerning possible use of EMI shielding coatings on aircraft fuel system components.
- Visited (R. Claus) NASA-LaRC Materials Division (Dr. Terry St. Clair, Dr. Joycelyn Simpson) on 28-30 October, in part to discuss potential use of NASA-LaRC high T_g polymers in ISAM processing.
- Discussions between Dr. R. Claus and Dr. Janet Sater, IDA, at NASA-LaRC, concerning program progress and proposed Phase II commercialization plans.
- Additionally, Dr. John Pazik, ONR, is tentatively scheduled to visit F&S and FEORC on Thursday, 13 November, 1997.
- Additionally, Dr. Gerard Orcel, Alcatel, is scheduled to visit from Paris on Tuesday, 25 November, to discuss possible transition of ISAM coating technology to optical fiber products.

Note that expenses for travel to visit individuals has been provided through cost-sharing by both Fiber Core Technologies (FCT) and Virginia Tech, and not by Phase I SBIR project funds. Additional support from FCT is summarized below.

Continued analysis and discussion with these and other individuals and groups indicates that among other possible properties, protective coating materials are required to have the following characteristics.

1. Large UV absorption to prevent degradation of polymer and polymer matrix composite (PMC) structural materials. Drs. McDaniel, St. Clair and Simpson at NASA-LaRC gave us information concerning degradation mechanisms in PMCs due to space exposure, and work with protective spin-coated thin-films in their lab. Dr. Charles Stein at Phillips Lab/Kirtland gave us information concerning space-charge effects that may alter degradation of space-based materials and showed us extensive laboratories for testing.
2. Small skin depth to allow effective electromagnetic interference (EMI) shielding. This requires a combination of large conductivity and permeability at specific electromagnetic frequencies. Dr. Nguyen at NRL and Dr. Shull at NIST both volunteered to independently characterize nanoparticle-based magnetic thin-film specimens for us. Dr. Shull has visited (26 September) to further cooperative efforts.
3. Resistance of surface adhesion and changes in properties to abrasion. Both Dr. St. Clair's group at NASA-LaRC and Dr. Cooper's group at WPAFB gave suggestions for MIL-SPEC testing of thin-film adhesion. These have been used during the current reporting period.
4. Resistance of surface adhesion and changes in properties to thermal exposure and thermal cycling.
5. Resistance of surface adhesion and changes in properties to mechanical stress.
6. Resistance of surface adhesion and changes in properties to water attack.

4.2 Developments in Nanoparticle and Self-Assembly Precursor Synthesis

During this Phase I program, F&S made substantial progress in the development of methods for 1) the controlled chemical-based synthesis of nanoparticle inorganic oxides, noble metals, and organic polymer-based active coating material precursors, 2) the formation of ionic aqueous solutions from these nanoparticles, and 3) their incorporation via self-assembly into functional thin-films and first-generation devices. The characteristics, performance and functionality of nanoparticle-based self-assembled coatings and electronic and optoelectronic device products depend critically on the species of nanoparticles, and their mean size, size distribution, and relative spatial orientation in the self-assembled thin-films. This section briefly outlines F&S' progress in each of these areas.

Accomplishments during the first five months of this program (May 1 – September 30, 1997) include the following items that are summarized in the three prior reports.

- Demonstrated ISAM coatings on different size and irregular shape substrates
- Demonstrated ISAM coatings on glass, optical fiber and single crystal Si

- Demonstrated ISAM coatings on polycarbonate substrate surfaces
- Synthesized and characterized TiO_2 and Fe_3O_4 nanoparticles
- Synthesized and characterized TiO_2 and Fe_3O_4 nanoparticle/polymer coatings
- Synthesized ZrO_2, Pt and Au nanoparticles
- Synthesized ZrO_2 cationic solutions; synthesized and characterized ionic self-assembled ZrO_2 nanocomposite thin-films
- Synthesized Al_2O_3 ionic solutions; synthesized ionic self-assembled Al_2O_3 nanocomposite thin-films
- Synthesized and characterized ionic self-assembled gold nanoparticle thin-films
- Synthesized polyhydroxylated fullerene derivative
- Synthesized sulfonic acid ring substituted polyaniline
- Investigated the incorporation of metallic nanoparticles into thin-film monolayers for property modification and enhancement
- Investigated the modification of solution salt concentration to control the thickness of each bilayer

During the last month of the program, the following additional progress was made toward the synthesis and characterization of novel nanoparticle solutions and thin-films.

4.2.1 Developments in ZrO_2 Nanoparticle Synthesis

Molecular level-ordered ZrO_2/polymer nanocomposite films were self-assembled on silicon substrates using varied ZrO_2 concentrations. The samples shown below in Figure 4-1 were used for ellipsometry measurements. The thickness of each bilayer of ZrO_2/polymer film is approximately 2 nm and increases linearly with the addition of each bilayer.

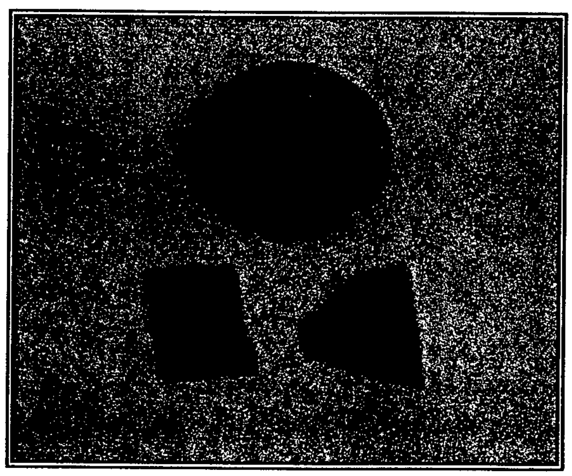


Figure 4-1. ZrO_2/Polymer ISAM Thin-Films Self-Assembled on Si substrates.

4.2.2 Developments in Al_2O_3 Nanoparticle Synthesis

Al_2O_3 Ionic Solution Characterization

The solution of Al_2O_3 nanoparticles was analyzed using the zeta potential system. The mean particle diameter was found to be 85.2 nm, with a zeta potential of 51.9 mV. The distributions are shown below in Figure 4-2 And 4-3. Particle size and size distribution plays an important role in determining absorption and emission characteristics via the quantum size effect. Zeta potential is the potential which is often most important in governing charge mediated particle interactions and thus the behavior of a suspension. Both are critical in ISAM technology.

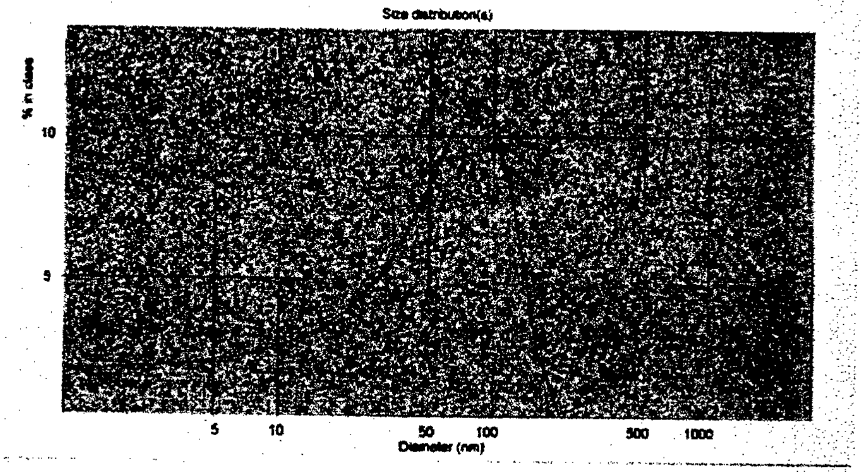


Figure 4-2. Particle Size Distribution of Al_2O_3 Nanoparticle Solution.

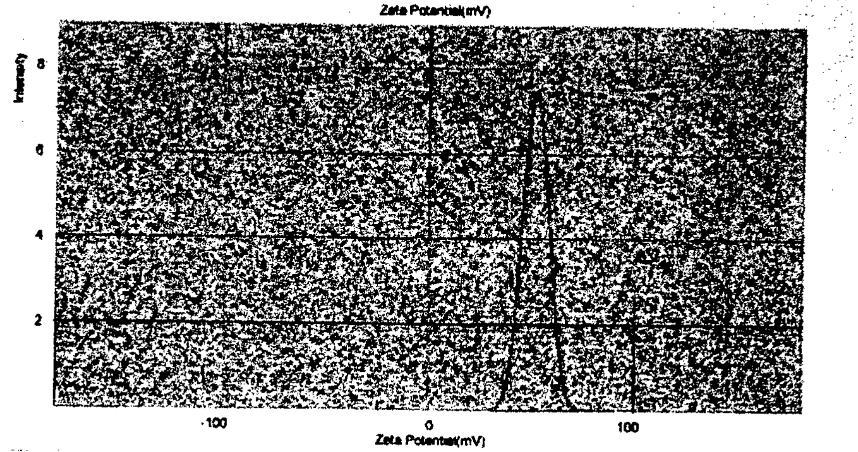


Figure 4-3. Zeta Potential Distribution of Al_2O_3 Nanoparticle Solution.

Al_2O_3 Nanocomposite Thin-Film Synthesis and Characterization

Molecular-level ordered Al_2O_3/polymer nanocomposite films were prepared using the layer-by-layer self-assembly process shown in Figure 4-4 below. This is the same method used previously for ZrO_2 nanocomposite films. Micron-thick nanocomposite films can be easily obtained by repetition of this method.

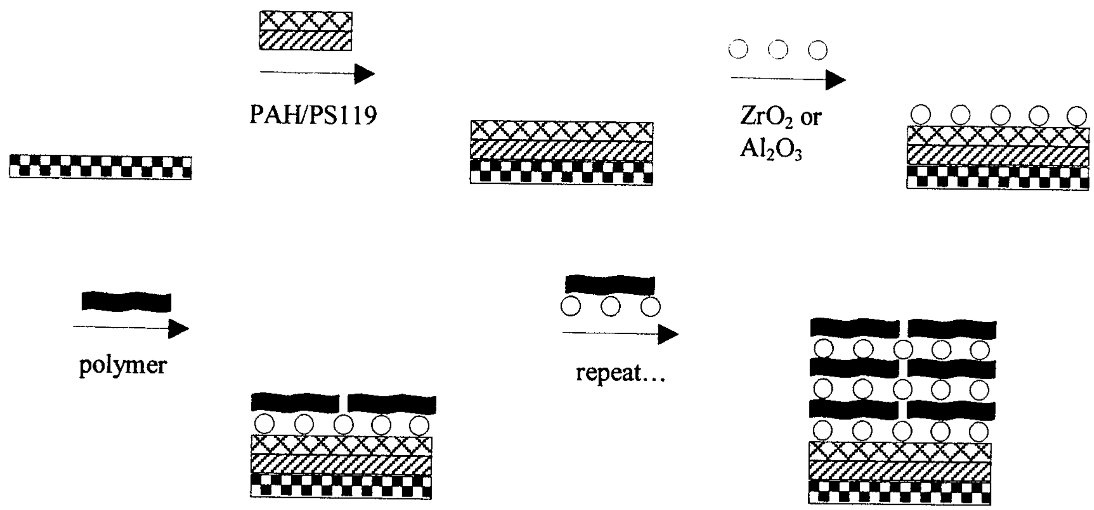


Figure 4-4. Self-Assembly of Al_2O_3/Polymer Nanocomposite Films.

Al_2O_3 from solutions of two different concentrations was deposited on several quartz substrates with a base of 4 bilayers of PAH/P-S119. Evaluation using a UV-Vis spectrophotometer confirmed that absorbance increased with the Al_2O_3 concentration. The UV-Vis spectra of two 20 bilayer films fabricated using 10 mg/mL and 40 mg/mL solutions are shown in Figure 4-5.

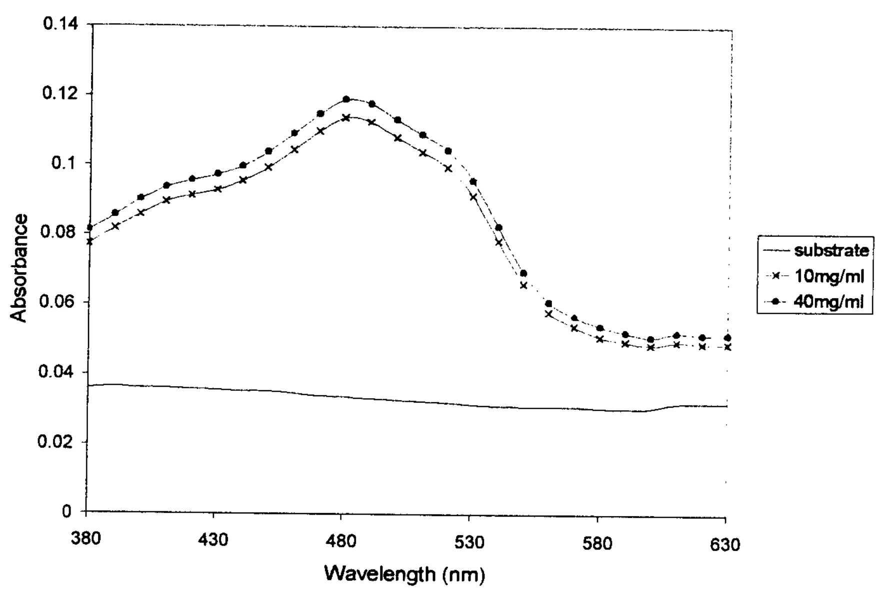


Figure 4-5. UV-Vis Absorbance of ISAM Films from Different Al_2O_3 Concentrations.

The thickness of each bilayer of Al_2O_3 /polymer film is approximately 5 Å, based on the ellipsometry measurements. Two Al_2O_3 coating samples are shown in Figure 4-6.

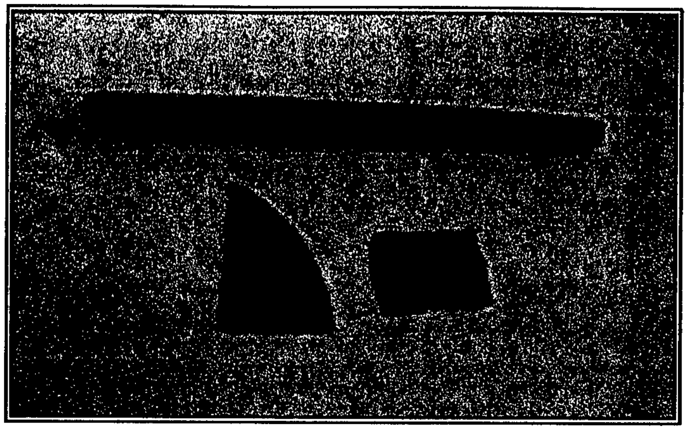


Figure 4-6. Al_2O_3/Polymer ISAM Thin-Films on Si Substrates.

4.2.3 Improvements to ISAM Processing

Using the ionic precursor solutions described above, we have investigated the incorporation of metallic nanoparticles into intermediate monolayers to enhance properties through controlled energy state coupling and resonance methods. This energy state enhancement is critically dependent on nanoparticle size and species and tuning of these properties could enable improved design of the conductivity, charge generation and separation, charge transfer, optical generation, and other properties in fabricated thin-film layers.

In an effort to model this effect, platinum nanoparticles in solution were analyzed using the zeta potential system. The smallest particle size measurable in the Zetasizer 3000 system is 1.0 nm. 90% of the platinum nanoparticles were less than 1.3 nm, with a mean zeta potnetial of 37.2 mV. The zeta potential distribution is shown below in Figure 4-7. Zeta potential is the potential which is often most important in governing charge mediated particle interactions and thus the behavior of a suspension.

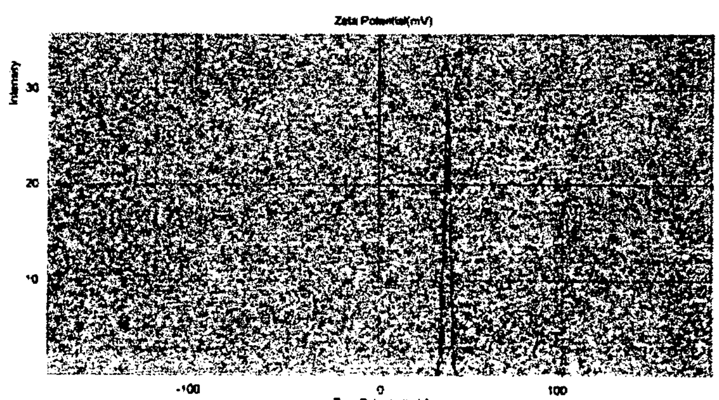


Figure 4-7. Zeta Potential Distribution of Platinum Nanoparticle Solution.

4.3 Characterization of Abrasion Resistance of Thin-Film Coatings

During the previous reporting periods of this Phase I program, F&S initiated measurements of abrasion resistance of polymer/dye and polymer/ZrO_2 ISAM coatings and extended these measurements for zirconia coatings, using a scotch tape test. These results are discussed in prior reports.

In this reporting period, efforts were focused on testing a new species of nanoparticles. The abrasion resistance of gold nanoparticle/polymer ISAM thin-films was investigated using both the Scotch tape test [13] and a moderate abrasion test. The moderate abrasion test was done by rubbing the coated surface with a pad of clean dry laundered cheesecloth that is affixed to the eraser of an abrasion tester. Two samples were self-assembled on ITO-coated glass substrates for testing: one 1-bilayer and one 60-bilayer, both shown in Figure 4-8.

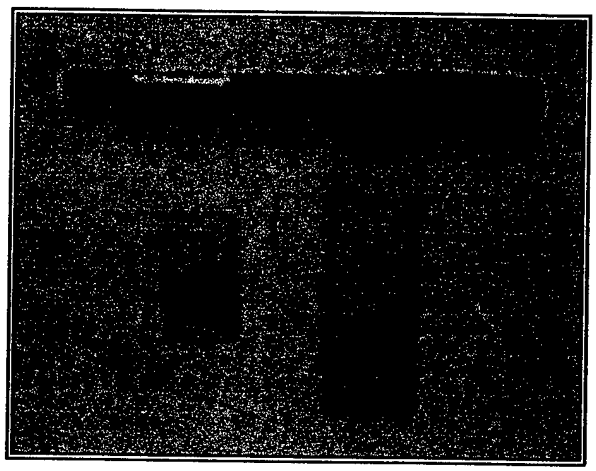


Figure 4-8. Au Nanoparticle Abrasion Test Specimens, 1 Bilayer (left) and 60 Bilayer (right).

Interesting results were observed. The absorbance of both samples changed very slightly after the Scotch-tape abrasion test. However, the change in the absorbance was less noticeable for the 60-bilayer sample, as shown in Figures 4-9 And 4-10. The thicker sample had more charged particles on the surface and a stronger attraction between the charges. Therefore, only a small number of particles were pulled out with the tape, resulting in a smaller change in absorbance. The single bilayer sample had much fewer particles compared to the 60-bilayer sample and a weaker attraction between the charges; therefore more particles were pulled out with the tape and the absorbance changed by a greater amount.

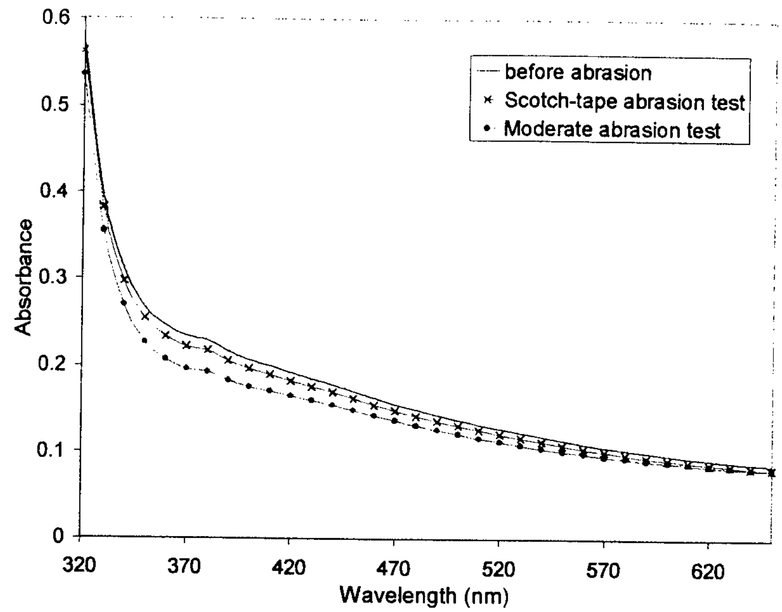


Figure 4-9. UV-Vis Absorbance of Abraded 1 Bilayer Au Nanoparticle/PSS Thin-Film.

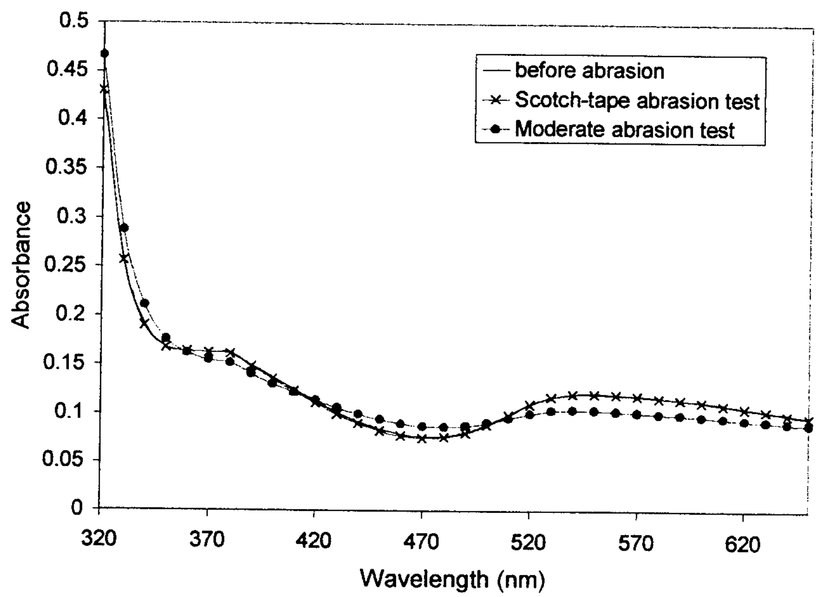


Figure 4-10. UV-Vis Absorbance of Abraded 60 Bilayer Au Nanoparticle/PSS Thin-Film.

The results of the moderate abrasion test showed a scratch mark on the 60-bilayer sample, but none on the 1-bilayer sample. This is shown in Figures 4-11 and 4-12. The particles were removed more uniformly from the surface of the 1 bilayer sample compared to the 60 bilayer. Following the test, the absorbance of the 60 bilayer sample exhibited scattering effects (see Fig 4-10), where at some wavelengths the absorbance was higher than the result from the Scotch-tape test and at others the value was lower.

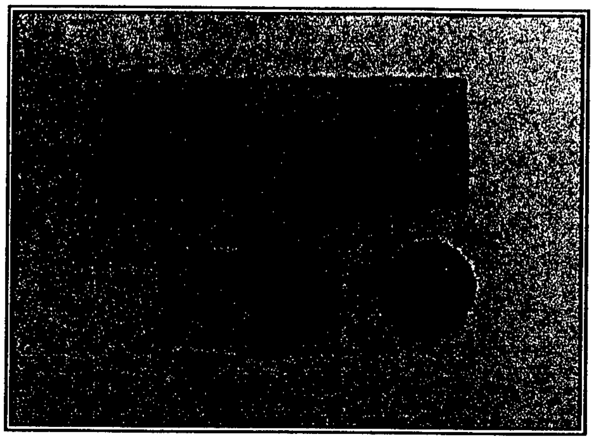


Figure 4-11. Test Specimens After Abrasion.

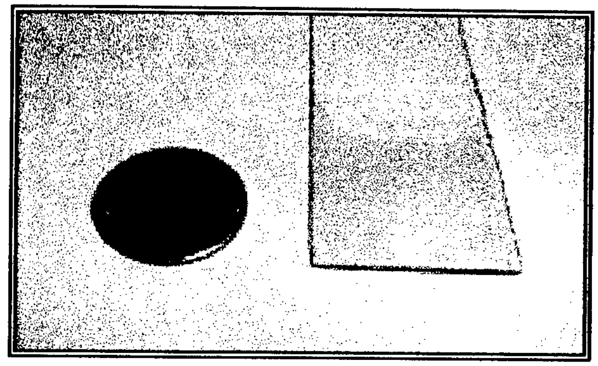


Figure 4-12. Close-up of Abrasion of 60 Bilayer Specimen; Note Discoloration Near End of Specimen.

4.4 Characterization of Hardness of Thin-Film Coatings

Abrasion testing has been performed as described in this and prior reports using both tape-pull and calibrated abrasion test kit equipment. F&S does not have equipment for measurement of the microhardness of nanoscale thin-films, but has sent fabricated samples away to independent testing laboratories for analysis. Initial good success with abrasion and related journal papers suggest that we should anticipate good microhardness performance as well. Data will be forwarded to the BMDO technical monitor as soon as possible after the end of this Phase I program, and will be important to the future development and scale-up of ultrahard coatings during Phase II.

4.5 Characterization of Coating Thermal Properties

Protective thin-film coatings for DoD and commercial components and systems must be able to withstand thermal cycling and thermal shock without degradation. As part of this task, we have investigated changes in the optical absorption properties of ISAM-formed thin-films before and after heating in air to temperatures up to 200 °C for periods up to 16 hours, and have observed negligible changes. This work was discussed in a prior report.

4.6 Characterization of Resistance to Water Attack of Thin-Film Coatings

Protective thin-film coatings should also resist changes in properties due to water attack. To study this potential effect, a polymer/organic dye ISAM thin-film was submerged in water for periods up to 21 hours; negligible degradation was observed in the UV-Vis absorbance spectrum. These results were discussed in a prior report.

4.7 Characterization of Coating Electrical and Magnetic Properties

Several nanoparticle/polymer thin-film systems have been considered for the implementation of conducting coatings during the Phase I program. Results for nanoparticle metal oxide/polymer multilayer thin-films have been discussed in prior reports.

I/V, C/V and four point probe conductivity measurements were made on ISAM-fabricated specimens to begin to investigate their charge transfer and related properties. All measurements were performed using equipment available in the Department of Materials Science and Engineering on campus at Virginia Tech which is shown in Figures 4-13, 4-14, and 4-15. Difficulties were encountered due to the condition and performance of the equipment, and the time required to develop sufficient practice with the measurement systems. For example, apparent leakage current problems plagued I/V measurement data at low current values. Further, initial measurement data obtained through C/V characterization is not yet fully understood due to the limited number of specimen tests performed on different samples having different nanoparticle constituents and molecular ordering. More comprehensive I/V and C/V testing of a wider range of specimens will be performed as part of Phase II program thin-film material optimization tasks. We will work cooperatively with Virginia Tech to repair their equipment, or will acquire the necessary equipment for our own product quality control use.

Conductivity data shown in this report suggests metallic oxide nanoparticle/polymer thin-film behavior is dominated in part by small size effects. Conductivity data varied from 12 to 450 ($1/\Omega\cdot cm$). Due to the measurements of coating uniformity obtained using other techniques, we do not feel that this observed variation is due to material inhomogeneity. As part of Phase II process optimization, we plan to complete extensive tests of conductivity to verify material behavior, and to analyze both metal nanoparticle and conducting polymer systems.

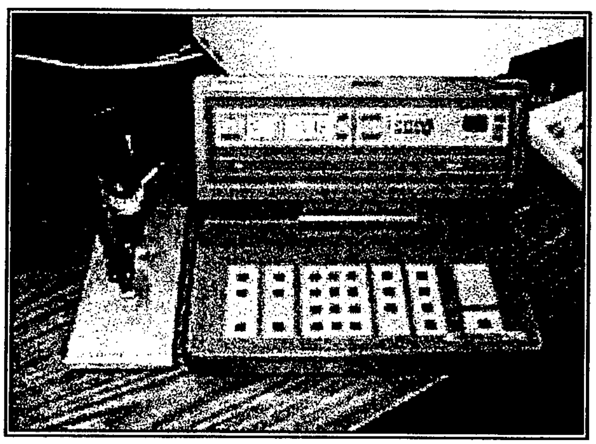


Figure 4-13. Loresta MCP T250/ Four-Point Probe.

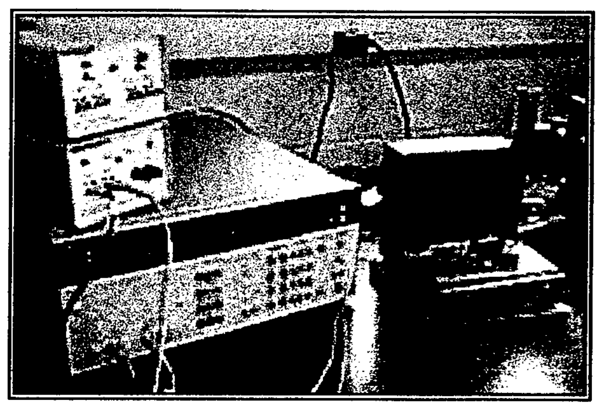


Figure 4-14. I/V Thin-Film Measurement Station.

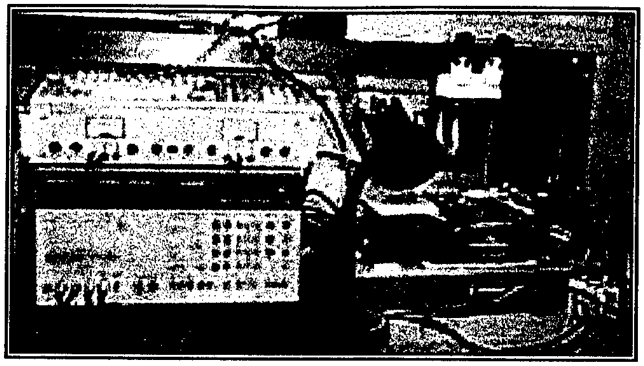


Figure 4-15. HP 4192A Impedance Analyzer Used for C/V Measurements.

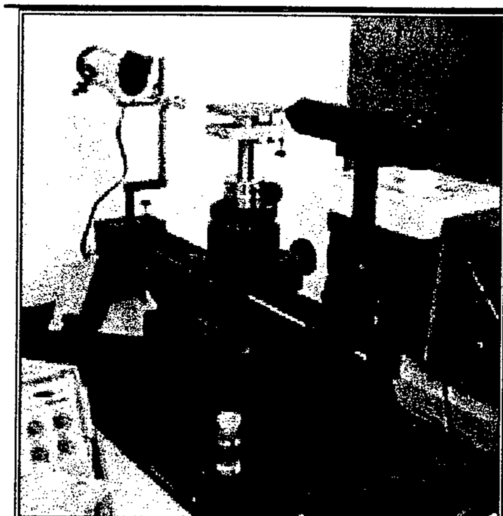
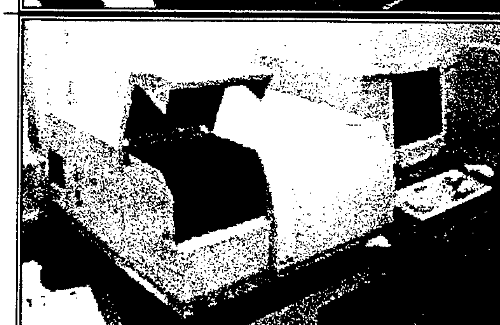
During the last month of the program, additional work has been performed to synthesize polyaniline precursors which will allow the ISAM fabrication of conducting polymer thin-films, of use for both conducting and EMI shielding as well as device interconnects. Difficulties have been encountered in the formation of homogeneous thin-films from the water soluble forms of polyaniline synthesized. We suspect that these difficulties are due to suboptimal combinations of concentration and pH, and are in the process of a parametric study of fabrication conditions to optimize material properties. The optimization of both the polyaniline precursor and ISAM processing will form two important tasks of the Phase II effort to be proposed to BMDO.

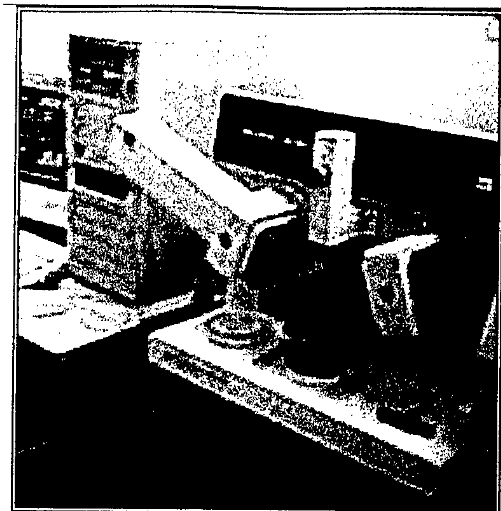
5.0 Discussion of Equipment and Logistics

This section briefly describes new equipment and F&S company logistics important to the success of the current Phase I program.

5.1 New Equipment and Importance to Program

New equipment for the fabrication and characterization of both inorganic nanoparticles and ISAM nanoparticle/polymer thin-films has been obtained by the research team during this Phase I program and is shown in the table below.

	Rame-Hart Contact Angle Goniometer • Measurement of the water contact angle on the outermost film surface
	Hitachi U-2001 Spectrophotometer • Characterization of UV-Vis absorbance characteristics of solutions and thin-films
	Hitachi F-4500 Fluorescence Spectrophotometer • Fluorescence characterization of optically active thin-film materials

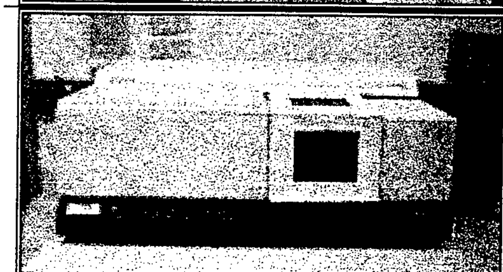


Rudolph Research Ellipsometer

- Measurement of thickness and refractive index

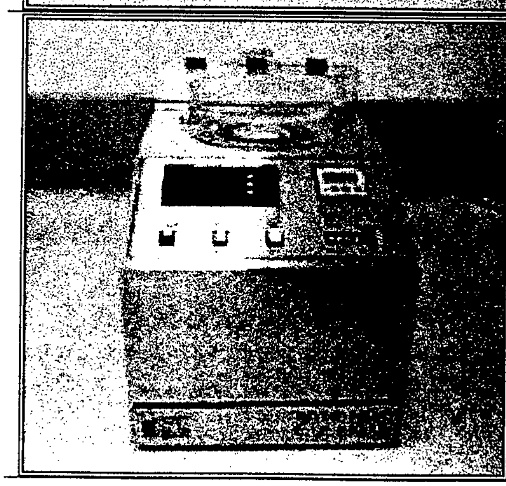
Edwards Evaporation and Sputtering System

- Fabrication of device electrode coatings and coatings prior to SEM and conductivity analysis



BioRad FTS 6000 FTIR Spectrometer

- Characterization both powder and liquid samples



International Crystal Laboratories Roto-Film Spincoating System

- Production of thicker films for comparison and in combination with ISAM thin-films

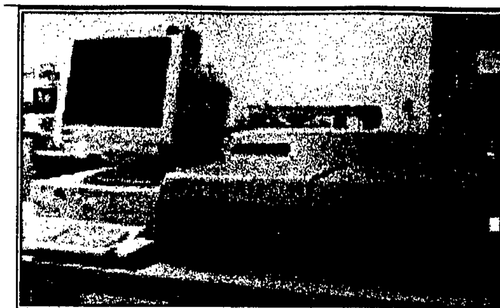
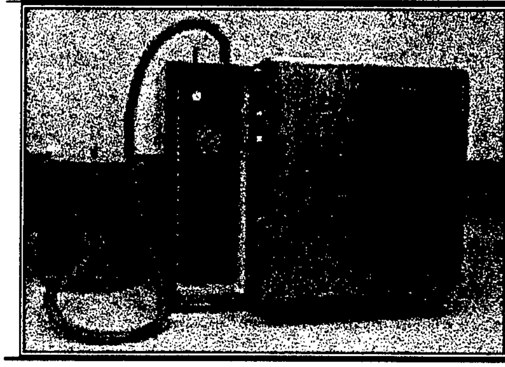
	Malvern Instruments Zetasizer 3000 • Investigation of particle size and distribution
	VWR Scientific Vacuum Oven • Conversion of precursor ISAM films to polymers

Table 5-1. New Characterization Equipment for Nanoparticles and ISAM Thin-Films.

An automated dipping machine should be delivered and available for rapid ISAM sample fabrication in November. Much of this equipment has been purchased on campus at Virginia Tech through an Army Research Office DURIP program monitored by Dr. John Prater.

5.2 New F&S Nanoparticle Coating, Material and Device Manufacturing Space

During this 6-month Phase I SBIR, F&S has expanded its manufacturing facility to include a new 2,000 square foot ISAM processing area; this area is completed and ready for use. Partial financial support for this new facility has been made available through commercialization funding from Fiber Core Technologies (FCT). FCT has worked with F&S on the commercialization of its off-the-shelf line of optical fiber sensors and instrumentation systems.

5.3 Relationship of This Program to Other Programs

This BMDO Phase I SBIR Program is directly related to other current programs in which the team members are involved. F&S has a separate BMDO Phase I program, monitored by Colin Wood at ONR, involving the development of ISAM-processed electronic and optoelectronic materials and devices. F&S is also working on a separate AFOSR Phase I SBIR, monitored by Dr. Charles Lee, for the development of NLO materials and devices through the ionic self-assembly of noncentrosymmetric molecular structures. These three SBIR programs share basic ISAM processing methods and measurement tools, although nanoparticle materials and commercial product applications are different.

F&S is in the process of negotiating a Phase I SBIR program with the Department of Transportation. This program will involve the development and commercialization of ISAM-fabricated protective coatings for large-scale civilian infrastructure, and infrastructure materials

incorporating high-performance nanoparticles. The anticipated overlap between the current BMDO program and this DoT program should be minimal and confined to developments of basic ISAM process chemistry.

F&S also is in the process of negotiating a Phase I SBIR program with DARPA. This program will involve the development and commercialization of frequency-tunable dielectric materials that may be used in RF and microwave devices and systems. Near-term demonstration articles will include discrete tunable capacitors for RF filters and distributed tunable transmission lines for tunable feed and antenna systems.

FEORC at Virginia Tech also has support through a DURIP equipment program from the Army Research Office for the acquisition of nanoparticle synthesis and characterization equipment as indicated above. Virginia Tech has provided 1:1 cash cost sharing for that program. Dr. John Prater in the Materials Division at ARO monitors the program.

6.0 Discussion of Product Commercialization Progress

During the Phase I program, F&S has analyzed the commercial markets that may be available for entry by ISAM-based protective and adaptive coatings. Details concerning market analysis have been considered as part of prior Phase I reports. We have specifically considered opportunities for large near-term commercial applications of passive, high-performance coating materials, as well as potential parallel applications in BMDO flight platforms and other DoD systems. DoD applications have been considered through visits to and from cognizant DoD program managers and researchers from major DoD contracting companies.

F&S' conclusions concerning the coating markets that may be addressed in the near-term using ISAM technology are as follows. Significant technical progress has been made during the Phase I program in the demonstration of the feasibility of using ISAM methods to create nanostructured inorganic/organic coatings with excellent physical and electromagnetic characteristics. In particular we have demonstrated the ability to fabricate low-cost coatings with 1) very strong UV absorption, 2) excellent abrasion and thermal resistance properties, 3) good conductivity and EMI shielding performance, and 4) adaptive electromagnetic property control.

As will be described in the Phase II proposal, F&S will build on its rapid development of such coatings, and will work in cooperation with Virginia Tech and several companies to commercialize coating systems as part of larger products. Specifically, F&S has talked cautiously and at length with several potential commercialization partners.

- In the UV and abrasion protection areas, we have discussed cooperative development with General Electric, specifically for application on aircraft canopies and moderately high temperature system components, Alcatel, a major worldwide manufacturer of optical fiber, cable and related products, Hunter Delatour, a U.S. manufacturer of approximately 10% of all custom-made plastic eyeglass lenses, and Mariah Vision, a small company that fabricates specialized optical component trains for entertainment systems.
- In the EMI shielding and conducting coating area, we have carefully discussed joint development with B.F. Goodrich Aerospace, in part for sensor instrumentation and fuel gaging

systems, and Southland Technologies, a major U.S. automotive component supplier, for the coating of automobile computer and personal communication chassis

With each of these representative partners, we will further develop production prototypes and begin manufacturing of early products.

Additionally, we have discussed related development with Lockheed-Martin Astronautics, Boeing and Northrop-Grumman, prime BMDO contractors, for the development of adaptive electromagnetic coatings for multifunctional space structures. Such development, while outside near-term commercialization targets, will be considered through the Phase II program as a lower priority commercialization task.

7.0 Future Plans

The current Phase I BMDO SBIR program ends on 31 October 1997. F&S has informed BMDO that it plans to submit a Phase II proposal. This proposal will be submitted to BMDO in the near future.

8.0 References and Bibliography

[1] Proceedings, DARPA Frequency Agile Materials for Electronics (FAME) Workshop, Herndon, VA, 15-16 May 1997

[2] Y. Liu and R. O. Claus, "Blue Light Emitting Nanosized TiO_2 Colloids," *J. Am Chem. Soc.*, vol. 30, no. 22, May 1997.

[3] Y. Liu, A. Wang and R. Claus, "Molecular Self-Assembly of TiO_2/Polymer Nanocomposite Films," *J. Phys. Chem. B* 1997, 101, p. 1385-1388.

[4] Y. Liu, A. Wang and R.O. Claus, "Ionic Self-Assembled Monolayer Multi-Layer Thin-Films," Proceedings SPIE Smart Structures & Materials Conference, San Diego, February-March 1997.

[5] Y. Liu, A. Wang and R. Claus, "Layer-by-Layer Electrostatic Assembly of Nanoscale Fe_3O_4 Particles and Polyimide on Silicon and Silica Surfaces," Proc. MRS Meeting, San Francisco, March 1997.

[6] J. R. Heflin, Y. Liu, C. Figura, D. Marciu and R. Claus, "Second Order Nonlinear Optical Thin Films Fabricated from Ionically Self-Assembled Monolayers," SPIE Annual Meeting (San Diego), August 1997.

[7] J. Schmidt et al., "Metal Nanoparticle/Polymer Superlattice Films: Fabrication and Control of Layer Structure," *Adv. Mater.* 1997 9, No. 1, p. 61-65.[8] Y. Liu, J. R. Heflin, W. Zhou and R. Claus,"Self-Assembled Nanoparticle-Based Multi-Layer Thin-Films and Devices," Proc. ARO Smart Materials Workshop, Blacksburg, August 1997.

[8] H. A. Macleod, ed., *Thin-Film Optical Filters*, 2nd ed., Macmillan, New York, 1986.

[9] P. McDaniel, Proc. MRS Spring Meeting, paper V 2.8 (San Francisco), March 1997; also personal discussion with P. McDaniel, NASA-LaRC Polymer Materials Branch.

[10] see for example, G. Burns, "Titanium Dioxide Dielectric Films Formed by Rapid Thermal Oxidation," *J. Appl. Phys.* **65** (5), 1 March 1989, p. 2095.

[11] E. Matikevic, M. Budnik and L. Meites, *J. Colloid Interface Science* 1977, *61*, 302.

[12] G. Decher and J. Schmitt, *Progr. Colloid Polym. Sci. 89*, p.160 (1992).

[13] D.S. Campbell in Chapter 12.3, *Handbook of Thin Film Technology*, L.I. Maissel and R. Glang (eds.), MacGraw Hill, New York (1970).

9.0 Publications and Presentations

The following are recent or current publications or presentations by the research team concerning the ISAM processing of nanoparticle thin-films.

Recent Publications

1. "Molecular Self-Assembly of TiO_2/Polymer Nanocomposite Films," Y. Liu, A. Wang and R.O. Claus, *J. Phys. Chem. B* 1997, 101, p. 1385-1388, February 1997.
2. "Ionic Self-Assembled Monolayer Multi-Layer Thin-Films," Y. Liu, A. Wang and R.O. Claus, Proceedings SPIE Smart Structures & Materials Conference, San Diego,
3. "Layer-by-Layer Electrostatic Assembly of Nanoscale Fe_3O_4 Particles and Polyimide on Silicon and Silica Surfaces," Y. Liu, A. Wang and R. Claus, Proc. MRS Meeting, San Francisco, March 1997.
4. "Blue Light Emitting Nanosized TiO_2 Colloids," Y. Liu and R. O. Claus, *J. Am Chem. Soc.*, vol. 30, no. 22, May 1997.
5. "Metallic and Ceramic Nanocomposites with Ionic Self-Assembled Nanoparticle Coatings," R. Claus, Y. Liu and K. Murphy, Proc. 4th Intl. Conf. on Composites Engineering (Kona, Hawaii), July 1997.
6. "Second Order Nonlinear Optical Thin Films Fabricated from Ionically Self-Assembled Monolayers," J. R. Heflin, Y. Liu, C. Figura, D. Marciu and R. Claus, SPIE Annual Meeting (San Diego), August 1997.
7. "Self-Assembled Nanoparticle-Based Multi-Layer Thin-Films and Devices," Y. Liu, J. R. Heflin, W. Zhou and R. Claus, Proc. ARO Smart Materials Workshop, Blacksburg, August 1997.
8. "Noncentrosymmetric Ionically Self-Assembled Thin Films for Second Order Nonlinear Optics," J. R. Heflin, Y. Liu and R.O. Claus, submitted to OSA Thin-Films Conference, Long Beach, CA, September 1997.
9. "Layer-by-layer electrostatic self-assembly of nanoscale Fe_3O_4 particles and polyimide precursor on silicon and silica surfaces," Y. Liu, A. Wang and R.O. Claus, *Appl. Phys. Lett. 71* (16), 20 October 1997.

Publications and Presentations Pending

10. "Self-Assembled Nanoparticle-Based Thin-Film Materials and Devices," R. Claus, seminar to be organized by Dr. Janet Sater, Institute for Defense Analyses (Alexandria, VA), November 21, 1997.
11. "Nanoparticle/Polymer Materials and Devices," Y. Liu and R. Claus, SPIE Smart Structures and Materials Conf., March 1998.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 31, 1997	Final Report (10/01/97 – 10/31/97))

4. TITLE AND SUBTITLE
"Protective Coatings for Space System Components Fabricated Using Ionic Self Assembled"

5. FUNDING NUMBERS
N00014-97-C-0227

6. AUTHORS

Mike Miller, Janjing Liu and Richard O. Claus

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

F&S, Inc.
2801 Commerce Street, Blacksburg, VA 24060
P.O. Box 11704, Blacksburg, VA 24062-1704

8. PERFORMING ORGANIZATION REPORT NUMBER
NVY-1S-2006 (Final)

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Self-assembled multi-layer thin-film fabrication methods offer unique opportunities to incorporate multiple functionalities into coatings for space system materials and structures as well as consumer products. Ionic self-assembled monolayer (ISAM) techniques in particular permit the flexible combination of inorganic and organic materials at the molecular level, allowing broad multifunctional tailoring of materials response through the selective incorporation and long-range ordering of specific molecules. ISAM processing of such coatings has additional advantages of simple manufacturing, processing at ambient temperature and pressure, and ability to produce coatings on a variety of substrate materials, including ceramics, metals, polymers and composites. The focus of this program is to quickly develop the fundamental nanoparticle and ISAM synthesis research so commercially viable protective coating and related products may be manufactured and commercialized. Specific near-term technical goals include demonstration over control of nanometer particle size, understanding the quantum behavior of such particles in ordered thin-films, and upscaling the thin-film process to large structural components.

14. SUBJECT TERMS
self-assembly, polymer, nanoparticle, monolayer, ionic, composites, coatings, thin-film

15. NUMBER OF PAGES
22

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	